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(54) Name of the invention: Alumina-Zirconia-Titania Type Grinding Material

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(54) Alumina-Zirconia-Titania Type Grinding Material

Detailed Description of the Invention

1. Name of the Invention

Alumina-Zirconia-Titania Type Grinding Material

2. Scope of the Claims of the Invention

- (1) Alumina-zirconia-titanium type grinding material that is a material obtained as zirconia and titania are added to alumina and melted, and then rapidly cooled, where then as another melting additive material yttrium oxide or rare earth type mineral ore material containing yttrium oxide are included.
- (2) Alumina-zirconia-titanium type grinding material according to Claim 1 of the claims of the present invention where the added amount of yttrium oxide is in the range from 0.05 weight % to 7 weight %, relative to the total amount of the alumina, zirconia, and titania.
- (3) Alumina-zirconia-titanium type grinding material according to Claim 1 of the claims of the present invention where the added amount of the yttrium oxide containing rare earth type ore material is in the range from 0.05 weight % to 7 weight %, relative to the total amount of the alumina, zirconia, and titania.

3. Detailed Explanation of the Invention

This invention is an invention about the improvement of the grinding (polishing) performance of alumina-zirconia-titania type grinding material.

Usually, the alumina-zirconia-type polishing particles are polishing particles that have been quickly expanded in their use as "snacking" of the steel type materials like specialty or stainless steel materials. Namely, compared to the alumina type polishing particles, they have excellent wear resistance and together with that breakage resistance etc., polishing properties, and the fact that under high pressure conditions, they demonstrate superior polishing strength, is the main factor. According to the invention reported in the description of the Japanese Patent Report Number Showa 48-35594, that has been invented previously by the authors of the present invention, an alumina-zirconia-titania material has been obtained that has a polishing performance that is even further increased and more superior than that.

Namely, it is a material where zirconia is added to alumina and together with that then titanium oxide is added in an amount that is in the range of 5 ~ 30 weight % relative to this zirconia amount, and then melted, and because of the fact that it is then quickly cooled, the phenomenon of the phase transformation back to the original zirconia is suppressed, and because of that the high temperature type tetragonal system crystalline phase remains present in an amount in the range of 25 ~ 30 % at normal temperatures, and due to that, it contributes to the increase in the wear resistance properties, breakage resistance properties, etc., polishing properties performance.

However, recently, there is a trend where the polishing methods have also constantly been changing, and the application of fine materials in the so-called heavy grinding field, and especially among those, the significant development of the technology of the change to the light grinding field within the heavy grinding, and also the use of the polishing materials for polishing relative to titanium alloys, has increased. A grinding material that is appropriate for this field is currently required, however, in this case, the required grinding performance is a performance that is higher than that of the above described alumina-zirconia-titania type grinding material, and especially, it is a material that cannot be a severe type of material, and the current status is that a grinding material with satisfactory grinding properties has not yet been obtained.

Namely, in order to be appropriate for the above-described application, it is necessary to suggest a grinding material where however it is stated it has a relatively high amount of zirconia, for example, a grinding material that is formed from a alumina-zirconia co-crystalline material of the type where the amount of zirconia is 40 %. However, in this case, even though it is an

alumina-zirconia-titania material obtained through the above-described titania addition, the ratio of the remaining existing high temperature type tetragonal crystal is extremely low, and the result from the addition is poor. Also, there have been the problems that the initial crystalline alpha-Al₂O₃, whose crystal size in the mixed crystalline material is a maximum of 20 microns, is separated at a level of 10 ~ 15 %, and because of that, the predetermined co-crystalline mixed material could not be obtained.

Then the goal of the present invention is to suggest an alumina-zirconia-titania type grinding material where in order that this material be good for application especially relative to heavy grinding, and especially to the light grinding, and then also, relative to titanium alloys, the remaining present amount of the tetragonal crystalline material is extraordinarily increased, and also, the coefficient of the separation of the original crystals of the alpha-Al₂O₃ is reduced, and because of that the grinding performance is significantly increased. And the characteristics of this material are the fact that it is an alumina-zirconia-titania type grinding material, where then as another additive material yttrium oxide or yttrium oxide containing rare earth ore material, is contained, and it is then called an alumina-zirconia-titania-yttria type grinding material.

Namely, as the additive materials, besides titania, yttrium oxide or yttrium oxide containing rare earth ore material are then added and mixed, and melted, and quickly cooled and by that, a grinding material is obtained that achieves well and satisfies the above described goal. And especially, it is a material where the added amount of the yttrium oxide or yttrium oxide containing rare earth ore material is within the range where it exceeds 0.5 weight % and is up to 7 weight % relative to the total amount of the alumina, zirconia, and titania, and where the zirconia tetragonal crystalline material is crystal separated at a remaining ratio that is in the range of 70 ~ 100 %. And not only that but also, within the same range, the ratio of the separation of the initial crystalline alpha-Al₂O₃ can be suppressed to a level below 5 weight %.

Moreover, even in the case when the added amount is higher than 7 weight % or below 0.05 weight %, the proportion of the remaining zirconia tetragonal crystal material shows a value that is relatively high compared to the previous technology, and also, the ratio of the separated initial alpha-Al₂O₃ has a trend where it is significantly suppressed. However, in the case where the added amount exceeds 7 weight %, this leads to the separation of

a cubic crystalline phase, which is not preferable from the point of view of the grinding performance. And in the case when the added amount is less than 0.05 weight %, significant results are not obtained and because of that the range where the added amount is higher than 0.05 weight % and it is up to 7 weight %, is most appropriate, and especially, it is most appropriate that the added amount is within the range of 1 ~ 5 weight %.

Moreover, even, relative to a grinding material that contains an alumina-zirconia co-crystalline material with a relatively small amount of zirconia, for example, 25 %, the same way as in the case of the above-described grinding material that is formed from an alumina-zirconia co-crystallized material that contains a relatively large amount of zirconia, the ratio of the remaining tetragonal crystalline phase zirconia is extremely high, and because of that, the volume change, which occurs at the zirconia transition point is small, and also, the remaining present tetragonal crystalline type zirconia maintains sufficiently its inner part energy, and it has been concluded that there is a trend of improvement of the properties, like good breakage resistance properties, etc.

After that, the practical implementation examples according to the present invention will be explained.

Moreover, as the yttrium oxide or yttrium oxide containing rare earth ore material, that are used in the practical implementation examples according to the present invention, the materials with the analyses values shown according to Table 1, were used.

Table 1

	1	2
	酸化イットリウム (wt%)	酸化イットリウムを含む 稀土類物質 (wt%)
Y ₂ O ₃	99.9	60
Fe ₂ O ₃	0.0015	0.013
Na ₂ O	0.0015	—
K ₂ O	0.0015	—
SiO ₂	0.001	0.05
La ₂ O ₃	—	<10
CaO ₂	—	<10
Nd ₂ O ₃	—	<10
Yb ₂ O ₃	—	6
Er ₂ O ₃	—	6.5
Sm ₂ O ₃	—	2

Headings in the table:

1. yttrium oxide (weight %), 2. rare earth ore material containing yttrium oxide (weight %).

Table 2:

1 2 3

試料番号	Y ₂ O ₃ 添加量 (wt%)	Al ₂ O ₃	ZrO ₂	TiO ₂	Y ₂ O ₃	Fe ₂ O ₃	SiO ₂	Na ₂ O
1	0	56.94	41.61	1.20	—	0.05	0.12	0.08
2	0.05	57.43	41.25	1.00	0.03	0.04	0.13	0.03
3	0.1	57.91	40.75	1.05	1.06	0.05	0.14	0.04
4	0.5	57.65	40.85	1.02	0.27	0.03	0.14	0.04
5	1	57.12	40.08	1.10	0.64	0.06	0.16	0.04
6	2.5	55.92	41.30	1.03	1.52	0.05	0.14	0.04
7	5	55.16	40.45	1.05	3.00	0.04	0.18	0.03
8	10	52.47	40.12	1.11	6.05	0.05	0.17	0.03

Headings in Table 2:

1. Material number, 2. Y₂O₃ added amount (weight %).

Practical Example 1

A compounding calculation was conducted so that the zirconia in the grinding particles became 40 %, and to 50 kg of Bayer method alumina (99.6 % Al₂O₃), 32.6 kg zirconia (96 % ZrO₂), 0.8 kg of titanium oxide (95 % TiO₂) which corresponds to 2.5 in weight % relative to the zirconia, were mixed and combined, and then, yttrium oxide (99.9 % Y₂O₃) was added in an amount of 0.05, 0.1, 0.5, 1, 2.5, 5, 10 weight % relative to the total amount of the above described three types of materials, and this was then melted using an electrical oven at 95 V, 300 kV, and after that, it was quickly solidified, and melt cast materials were obtained for each addition amount.

Moreover, for the sake of a comparison, a melt cast material where the addition amount of the yttrium oxide was 0 weight %, was also cast.

The values obtained from the analysis of this cast materials, are shown according to the presented in table 2.

After that, the obtained cast material was repeatedly crushed by using an impeller breaker and a crusher, and particle sizes of # 24, and # 60, as determined according to the procedures of the JISR-6001, were withdrawn and obtained.

The ratio of the zirconia crystalline phases of the particle material group # 24, determined by X-Ray Diffraction analysis, is shown according to the presented in Table 3.

Table 3:

試験番号	立方晶ZrO ₂ (%)	四面晶ZrO ₂ (%)	立方晶ZrO ₂ (%)
1	30.1	69.9	0
2	32.1	67.9	0
3	70.7	29.3	0
4	87.9	12.1	0
5	100	0	0
6	100	0	0
7	100	0	0
8	45.8	0	14.2

Headings in table 3:

1. Experimental Material number, 2. tetragonal ZrO₂ (%), 3. monoclinic crystal phase ZrO₂ (%), 4. cubic crystal phase ZrO₂ (%).

As it is clear from the results of the X-Ray Diffraction Analysis, if yttrium oxide is added, compared to the alumina-zirconia-titania type grinding particles according to the previous technology where there is no such addition (Experimental material number 1), it is concluded that there is a trend of a significant increase of the tetragonal crystalline phase amount. And especially, it was confirmed that by the addition of an additive amount in the range of 1 ~ 5 weight %, there was a 100 % tetragonal crystal phase

crystal separation. Also, in the case of the addition of 0.05 weight %, there was a corresponding trend of increase of the amount of the separated tetragonal crystal phase, however, there was no significant difference with the previous technology material, and also, if the added amount exceeded 10 weight %, a separation of a cubic crystalline phase was observed.

On the other hand, at the time when the separation of the initial alpha-Al₂O₃ of for example a material according to the previous technology (Experimental material 1) and material where the added amount of the yttrium oxide was 0.5 weight % (Experimental material 3), with the same # 24 particle size, was observed by using a metal observation microscope, the results that are shown according to the presented in Figure 1 (A), (B) and Figure 2 (A), (B), were obtained. In each case, the magnification was x 100, and Figure 1 (A), (B), represents an enlarged microphotograph of the Experimental material 1, and its model diagram, and Figure 2 (A), (B), represents an enlarged microphotograph of the Experimental material 3, and its model diagram.

Moreover, in both figures, 1 represents the alumina-zirconia co-crystalline material, and 2 - the alpha-Al₂O₃ initial crystals.

As it is clear from Figure 1 and Figure 2, in the case of the material with the addition of the yttrium oxide, the separation of the initial alpha-Al₂O₃ crystals was significantly suppressed, and it was confirmed that the predetermined co-crystalline mixed material, was obtained.

Moreover, it was confirmed that the same trend exists in the case of the other materials where yttrium oxide has been added, however, in the case when the added amount was 0.05 weight %, the separated alpha-Al₂O₃ was at a level of 10 %, and because of the fact that the material according to the previous technology had a level in the range of 10 ~ 15 %, this trend was almost negligible.

After that, grinding performance tests were conducted relative to the materials with the particle size of # 60.

Namely, a polishing belt was prepared and a polishing test was conducted and the results from that test are shown according to the presented in Table 4.

Moreover, the polishing test was conducted as the size of the belt used was 100 x 2500 m/m, and as the material subject to the polishing SUS-304 was used, and the belt speed was set at 150 m/minute, and the pressure was at 5 kg, and a 10 minute polishing was conducted. Table 4 is a table that shows the comparison of the cumulative mass polished amounts that were obtained by this polishing.

Also, the number in the parentheses shows the comparative value when the case of the material obtained according to the previous technology (Experimental material 1) is set as 100.

Table 4:

試料番号	累積研削量 (g)
1	94.4 (Ratio 100)
2	95.0 (" 100)
3	113.0 (" 120)
4	115.7 (" 123)
5	119.2 (" 126)
6	120.6 (" 128)
7	120.4 (" 127)
8	96.0 (" 101)

Headings in the table:

1. Experimental material number, 2. cumulative mass polished amount (g).

Also, the curve line (a) in Figure 3 represents a graph where the cumulative mass polished amounts presented in Table 4, have been plotted.

As it is clear from the above described Table 4 and Figure 3, it has been confirmed that in the case of the co-crystalline grinding particles where yttrium oxide has been added, an extremely excellent polishing strength has been demonstrated compared to the material according to the previous technology where yttrium oxide has not been added.

In this connection, these results are results that correspond to the ratios of the zirconia tetragonal crystalline lattice crystal material, and in the case of the material where the addition amount was 0.05 weight %, there was no significant difference with the material according to the previous technology; and also, in the case when the added amount exceeded 10

weight %, a trend down from the material according to the previous technology was observed due the accompanying separation of cubic crystalline phase material.

However, the addition of the yttrium oxide significantly increases the polishing strength as a total, and not only that, but also, when it is considered that this test results represent only a comparison at the time when a 10 minute polishing has been completed, it is clear that a material is obtained which during the use in practice contributes to the improvement and to achieving extremely excellent polishing performance.

Practical Example 2

A compounding calculation was conducted so that the zirconia in the grinding particles became 40 %, and to 50 kg of Bayer method alumina (99.6 % Al₂O₃), 32.6 kg zirconia (96 % ZrO₂), 0.8 kg of titanium oxide (95 % TiO₂) which corresponds to 2.5 in weight % relative to the zirconia, were mixed and combined, and then, three types of yttrium oxide containing rare earth mineral ore (the materials with analyses values shown according to the presented in Table 1) was added in an amount of 1, 2.5, 5 weight % relative to the total amount of the above described three types of materials(zirconia, alumina, titania), and this material was then melted using an electrical oven at 95 V, 300 kV, and after that, it was quickly solidified, and melt cast materials were obtained for each addition amount.

The values obtained from the analysis of this cast materials, are shown according to the presented in table 5. Moreover, the experimental material number 1 is the same as that in the case of the Practical Example 1 and it is a material according to the previous technology where yttrium oxide has not been added.

Table 5:

2
5

試験 番号	Y ₂ O ₃ を 含む稀少な 礦物の添加量 (wt%)	Al ₂ O ₃	ZrO ₂	TiO ₂	Fe ₂ O ₃	SiO ₂	Na ₂ O	
1	0	56.94	41.61	1.20	—	0.05	0.12	0.08
2	1	57.30	40.97	1.04	0.42	0.05	0.13	0.03
10	2.5	56.56	41.04	1.09	1.05	0.06	0.10	0.04
11	5	56.19	40.33	1.12	2.11	0.06	0.17	0.03

Headings in Table 5:

1. Experimental material Number, 2. Added amount of yttrium oxide containing rare earth mineral ore (weight %).

*Rare earth type other than Y₂O₃.

After that, the obtained cast material was repeatedly crushed by using an impeller breaker and a crusher, and particle sizes of # 24, and # 60, as determined according to the procedures of the JISR-6001, were withdrawn and obtained.

The ratio of the zirconia crystalline phases of the particle material group # 24, determined by X-Ray Diffraction analysis, is shown according to the presented in Table 6.

Table 6:

1 2 3 4

試料番号	正方晶ZrO ₂ (%)	四面晶ZrO ₂ (%)	立方晶ZrO ₂ (%)
1	30.1	69.9	0
9	96.4	3.6	0
10	100.0	0	0
11	100.0	0	0

Headings in table 6:

1. Experimental Material number, 2. tetragonal ZrO₂ (%), 3. monoclinic crystal phase ZrO₂ (%), 4. cubic crystal phase ZrO₂ (%).

As it is clear from the results of the X-Ray Diffraction Analysis, if yttrium oxide containing rare earth mineral ore is added, the same way as in the case of the addition of yttrium oxide, compared to the alumina-zirconia-titania type grinding particles according to the previous technology where there is no such addition (Experimental material number 1), it is concluded that there is a trend of a significant increase of the tetragonal crystalline phase amount.

And it was confirmed that by the addition of an additive amount in the range of 2.5 ~ 5 weight %, there was a 100 % tetragonal crystal phase crystal separation.

After that, grinding performance tests were conducted relative to the materials with the particle size of # 60.

The experimental conditions are the same as those in the case of the Practical Example 1 and the results from that test are shown according to the presented in Table 7.

Table 7:

Table 7	
試料番号	累積研削量 (g)
1	94.4 (Ratio 100)
9	118.7 (Ratio 126)
10	120.0 (Ratio 127)
11	119.2 (Ratio 126)

Headings in the table:

2. Experimental material number, 2. cumulative mass polished amount (g).

Also, the curve line (b) in Figure 3 represents a graph where the cumulative mass polished amounts presented in Table 7, have been plotted.

As it is clear from the above described Table 7 or Figure 3, it has been confirmed that in the case of the co-crystalline grinding particles where yttrium oxide containing rare earth mineral ore has been added, the same way as in the case described in the Practical Example 1 where yttrium oxide was added, an extremely excellent polishing strength has been demonstrated for the obtained co-crystalline grinding particles.

Practical Example 3

A compounding calculation was conducted so that the zirconia in the grinding particles became 40 %, and to 50 kg of Bayer method alumina (99.6 % Al₂O₃), and to 32.6 kg zirconia (96 % ZrO₂), 1.7 and 4.9 kg of titanium oxide, which corresponds to 5 and 15 weight % relative to the zirconia, were mixed and combined, and then, yttrium oxide was added in an

amount of 0.5 weight % relative to the total amount of the above described three types of materials. And for this material, the results from the analyses of the cast material, the ratio of the zirconia crystalline lattice types according to the X-Ray Diffraction for the particle size # 24, and the cumulative mass polished amount for the particle size # 60, were measured.

These results are correspondingly shown according to the presented in Table 8, Table 9 and Table 10.

Moreover, for the sake of a comparison, the values in the case when there was no addition of yttrium oxide regarding the material where 2.5 weight % of titanium oxide was added, and the materials with the corresponding titania addition amounts, are also reported.

Also, in each case the testing methods are the same as those reported according to the Practical Example 1 and the Practical Example 2.

Table 8:

試料 番号	Ti O ₂ 追加量 (%)	Y ₂ O ₃ 追加量 (w%)	Al ₂ O ₃	Zr O ₂	Ti O ₂	Y ₂ O ₃	Fe ₂ O ₃	Si O ₂	Na ₂ O
1	2,5	0	56,94	41,61	1,20	—	0,05	0,12	0,00
4	2,5	0,5	57,65	40,85	1,02	0,27	0,03	0,14	0,04
12	5	0	57,06	40,63	2,06	—	0,03	0,18	0,04
13	5	0,5	56,78	40,71	2,04	0,25	0,04	0,15	0,03
14	15	0	54,16	39,72	5,91	—	0,03	0,14	0,04
15	15	0,5	53,41	40,24	5,83	0,29	0,04	0,15	0,04

Headings in table 8:

1. Experimental material number, 2. TiO₂ added amount (%), 3. Y₂O₃ added amount (%).

Table 9:

試料番号	正方晶 Zr O ₂ (%)	四面晶 Zr O ₂ (%)
1	30,1	69,9
4	87,9	12,1
12	33,0	67,0
13	90,2	9,8
14	34,2	65,8
15	93,6	6,4

Headings in Table 9:

1. Experimental Material number, 2. tetragonal ZrO₂ (%), 3. monoclinic crystal phase ZrO₂ (%).

Table 10:

試料番号	累積研削量 (g)		
	1	2	3
1	94.4	(Ratio 100)	
4	115.7	(*	123)
12	95.0	(*	100)
13	112.5	(*	119)
14	92.0	(*	97)
15	117.3	(*	124)

Headings in Table 10:

1. Experimental material number, 2. cumulative mass polished amount (g).

As it is clear from the tables, it is shown that together with the increase of the addition amount of the titanium oxide, there is a trend of increase of the ratio of the remaining present tetragonal crystalline phase ZrO₂, however, to that, also, by the addition of the yttrium oxide, a significant increase trend was observed.

Practical Example 4

The materials obtained as compounding calculations were conducted so that the zirconia in the grinding particles became 25 % and 32 %, and relative to 50 kg and together with that 24.5 kg of Bayer method alumina (99.6 % Al₂O₃), and 16.6 kg and together with that 11.5 kg of zirconia (96 % ZrO₂), correspondingly as weight percent, 0, 2.5, 5, 10, 15, 20, 30 and 40 % of titanium oxide (95 % TiO₂) were added, and the materials where compounding calculations were conducted so that the zirconia in the grinding particles became 25 %, and where relative to 50 kg of Bayer method alumina (99.6 % Al₂O₃); and 16.6 kg of zirconia (96 % ZrO₂), correspondingly as weight percent, 0, 5, 10, 15, 20, 30 and 40 % of titanium oxide (95 % TiO₂) were added, and then yttrium oxide was correspondingly added in an amount of 0.5 weight % relative to the total amount of the above described three types of materials, were correspondingly then melted by an arc heat using an electrical oven, and after that, it was quickly solidified, and these materials were then made into particles by following the usual grinding

particle manufacturing methods, and they were made into JIS #12 grinding particles.

These materials, namely, relative to the types without the yttrium oxide addition, which contain 25 % zirconia and 32 % zirconia, and the type where yttrium oxides has been added and which contains 25 % zirconia, the break resistance measurement test was conducted. For the break resistance measurement test the single particle break strength was used. In this method, the experimental material is granulated to a particle size in the range of 1680 ~ 2000 microns, and by the shrinkage method it is made into a small experimental material, and from within that sample, randomly, 100 units are taken out, and these are measured for their pressure resistance strength one by one, by using a 2 ton amsura compressing equipment. The average value of these measurements was used as the value for the single particle break pressure strength.

The single particle break pressure strength of these grinding particles is shown according to the presented in Table 11 and the relationship between the single particle break pressure strength and the TiO_2/ZrO_2 ratio, is presented in Figure 4.

Table 11:

試験番号	タイプ	TiO ₂ /ZrO ₂ (%)							
		0	2.5	5	10	15	20	30	40
10	Y ₂ O ₃ 無添加 ZrO ₂ 25% タイブ	46.0	48.8	51.8	61.0	60.0	58.9	52.2	46.7
17	Y ₂ O ₃ 無添加 ZrO ₂ 32% タイブ	46.3	47.5	53.8	63.0	63.3	62.0	49.3	46.0
18	Y ₂ O ₃ 無添加 ZrO ₂ 25% タイブ	48.1	—	55.8	64.7	64.2	63.3	54.1	48.0

Headings in Table 11:

1. Experimental material number, 2. type, 3. type without addition of Y_2O_3 , and 25 % ZrO_2 , 4. type without addition of Y_2O_3 and with 32 % ZrO_2 , 5. type with the addition of Y_2O_3 and with 25 % ZrO_2 .

As it is clear from the presented in Figure 4, in the case of any of these types of materials, when the ratio TiO_2/ZrO_2 , expressed as weight %, is within the range of 10 ~ 20 %, the strength shows a maximum value, and when the ratio becomes 40 %, there is a decrease. And especially, in the case of the material where yttrium oxide has been added, it was confirmed, naturally, that the type of material where the amount of the ZrO_2 was 25 % is a material which demonstrates an especially excellent break resistance performance compared that in the case when 32 % of zirconia has been added.

As described here above, in the case of the present invention, it is an invention about an alumina-zirconia-titania type grinding material, that is formed as to alumina, zirconia and titania are added and melted, and then quickly cooled, and then, as another melt additive material, yttrium oxide or yttrium oxide containing rare earth mineral ore is contained, and by that, it becomes a material where the maximum remaining zirconia tetragonal crystalline phase is 100 %, and also, even though it is a grinding material that is formed from an alumina-zirconia co-crystalline material with a relatively high amount of zirconia, the amount of the separated (precipitated) initial crystals of the alpha- Al_2O_3 is suppressed to less than 5 %, and because of that it is possible to suggest a material which has a significantly improved grinding performance.

Consequently, it is a material that can be used appropriately in heavy grinding also, and especially, in its light grinding field, and also then, it can be appropriately used relative to titanium alloys.

Also, even though it is an alumina-zirconia type grinding material that contains a relatively small amount of zirconia, compared to the materials according to the previous technology, it is a material whose break resistance strength etc., properties are further improved.

4. Brief Explanation of the Figures

Figure 1 (A), (B), represent the enlarged microphotograph and the model type diagram of the obtained according to the previous technology alumina-zirconia co-crystalline mixed material, which has no added yttrium oxide (Experimental material number 1).

Figure 2 (A), (B), represent the enlarged microphotograph and the model type diagram of the obtained according to one practical example of the present invention alumina-zirconia co-crystalline mixed material, which has added yttrium oxide (Experimental material number 3).

Figure 3 is a diagram showing the relationship between the added amount of yttrium oxide etc., which is found in the grinding material with added yttrium oxide and added yttrium oxide containing rare earth mineral ore, according to the same practical example and another practical example, and the cumulative mass polished amount.

Figure 4 is a diagram showing the relationship between the added amount of the titanium oxide found in the grinding material with relatively low zirconia amount and the single particle pressure break strength.

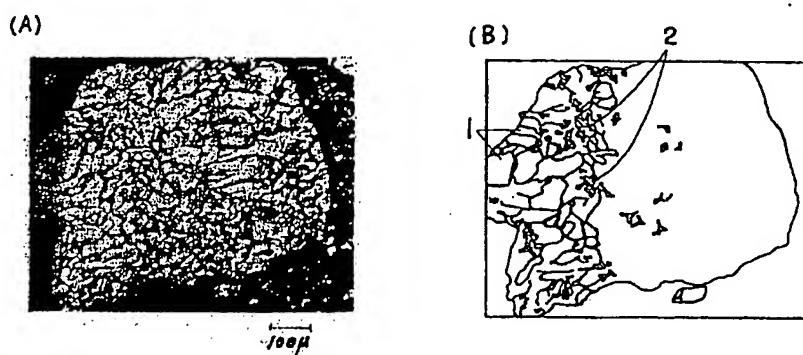


Figure 1: (A) and (B)

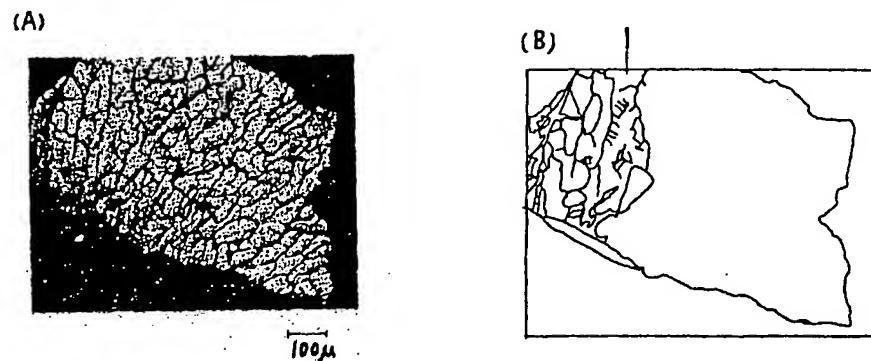


Figure 2: (A) and (B)

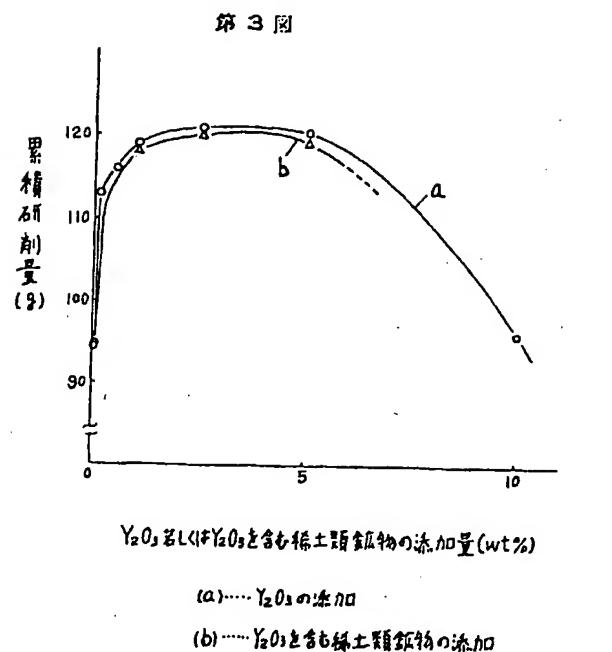


Figure 3:

On the vertical axis – cumulative mass polished amount (g)

On the horizontal axis – added amount of Y₂O₃ or Y₂O₃ containing rare earth mineral ore (weight %)

(a).....Y₂O₃ added amount

(b).....Y₂O₃ containing rare earth mineral ore added amount

第4図

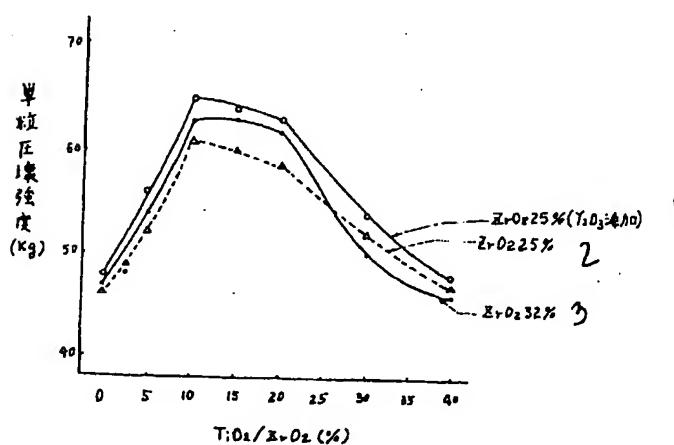


Figure 4:

On the vertical axis – single particle pressure break strength (kg)
On the horizontal axis – TiO₂/ZrO₂ (%)

1. ZrO₂ – 25 % (no Y₂O₃ added)
2. ZrO₂ – 25 %
3. ZrO₂ – 32 %

Patent Assignee: Nippon Kenmazai Kogyo KK

Translated by Albena Blagev ((651)735-1461 (h), (651) 704-7946 (w))

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⑯ アルミナージルコニアーチタニア系研削材

⑯ 発明者 谷口正明

堺市石津北町90番地日本研磨材
工業株式会社内

⑯ 特願 昭58-102289

⑯ 発明者 津田幸二

堺市石津北町90番地日本研磨材
工業株式会社内

⑯ 出願 昭58(1983)6月7日

⑯ 出願人 日本研磨材工業株式会社
堺市石津北町90番地

⑯ 発明者 岩田昭

⑯ 代理人 弁理士 大島泰甫

堺市石津北町90番地日本研磨材
工業株式会社内

⑯ 発明者 玉巻雅弘

堺市石津北町90番地日本研磨材
工業株式会社内

明細書

1. 発明の名称

アルミナージルコニアーチタニア系
研削材

2. 特許請求の範囲

(1) アルミナにジルコニア及びチタニアを添加溶融し、急冷してなるアルミナージルコニアーチタニア系研削材において、さらに他の溶融添加物として酸化イットリウム又は酸化イットリウムを含む粘土類鉱物を含有するアルミナージルコニアーチタニア系研削材。

(2) 酸化イットリウムの添加量が、アルミナ、ジルコニア、及びチタニアの全量に対し 0.05 wt % を超え 7 wt % に至る特許請求の範囲第 1 項記載のアルミナージルコニアーチタニア系研削材。

(3) 酸化イットリウムを含む粘土類鉱物の添加量が、アルミナ、ジルコニア及びチタニアの全量に対し 0.05 wt % を超え 7 wt % に至る特許請求の範囲第 1 項記載のアルミナージルコニアーチタニア系研削材。

ア系研削材。

3. 発明の詳細な説明

この発明はアルミナージルコニアーチタニア系研削材における研削性能の改良に関するものである。

一般にアルミナージルコニア系砥粒は、ここ数年間において特殊鋼やステンレス鋼等の鉄鋼材料のスナッキング用として急速に伸びてきた砥粒である。すなわちアルミナ系砥粒に比して耐摩耗性並びに抗破砕性等の研削性能に優れ、高圧下において優秀な研削力を発揮することがその主因であるが、本発明者が先に開示した特公昭48-35594号公報所載の発明では、それにも拘らずさらに一層すぐれた研削性能を具備するアルミナージルコニアーチタニア系研削材を提供し得たものであった。

すなわち、アルミナにジルコニアを加えるとともに、そのジルコニア量に対し 5 ~ 30 wt % の酸化チタンをさらに添加して溶融し、急冷するというもので、ジルコニア本来の転移現象に着目し、

高温型正方晶結晶を常温において25~30%程度残存させ、もって耐摩耗性、抗破碎性等の研削性能の向上に寄与せしめたものであった。

ところで近時では研削方法も次第に変化する傾向にあって、重研削という分野においても細分化され、その中でも特に重研削の中の軽研削分野への転換が技術の進歩に従い顕著になりつつある外、チタン合金に対する研削といった研削材上新分野への応用も増大しつつある。このような中にあってこれらの分野に対し良好に適応する研削材が今日とみに要求されるところであるが、この場合、要求される研削性能は前述アルミナージルコニアーチタニア系研削材にも増して更にスピアーナものとならざるを得ないものがあり、未だ満足できる研削材を得るに至っていないのが現状である。

すなわち上記のごとき用途に適応させるためには、どちらかといえばジルコニア量を比較的多量とした例えはジルコニア量40%タイプのアルミナージルコニア共晶体からなる研削材を提供する必要があるが、この場合では、前述のチタニア添

加によるアルミナージルコニアーチタニア系研削材であっても高温型正方晶結晶の残存率は未だ極めて低く、添加効果は乏しいものであり、また結晶混合物中に結晶の大きさが max 20 μm もある初晶の α -Al₂O₃ が 10~15% 程度の比率で析出することから、所定の共晶混合物を得られないといった問題点を有していたものである。

そこでこの発明の目的とするところは、重研削の中でも特にその軽研削に対し、またさらにチタン合金に対して格別に良好に適応して使用することができるようとするため、正方晶結晶の残存率を飛躍的に高め、かつ初晶の α -Al₂O₃ の析出率を減少させ、もって研削性能が一段と向上したアルミナージルコニアーチタニア系研削材を提供しようとするところにあり、その特徴とするところは、アルミナージルコニアーチタニア系研削材において、さらに他の添加物として酸化イットリウムまたは酸化イットリウムを含む稀土類鉱物を含有させた、いわばアルミナージルコニアーチタニアーチタニア系研削材としたところにある。

すなわち添加物としてチタニアの外、酸化イットリウムまたは酸化イットリウムを含む稀土類鉱物をさらに添加混入して溶融し、急冷化することにより上記目的を十分かつ良好に達成した研削材を得たものであって、特に酸化イットリウムまたは酸化イットリウムを含む稀土類鉱物の添加量が、アルミナ、ジルコニア及びチタニアの全量に対して 0.05 wt% を超え 7 wt% に至る範囲内においては、ジルコニアの正方晶結晶を 70~100% の残存率で晶出させることができたものであり、しかも同範囲内においては初晶の α -Al₂O₃ の析出率を 5 wt% 以下に抑えることができたものである。

なお無論 7 wt% 以上もしくは 0.05 wt% 以下の添加量であってもジルコニア正方晶結晶の残存率は従来に比して比較的大きな効果を示し、かつ初晶の α -Al₂O₃ の析出率を若干抑制する傾向はあるが、7 wt% 以上の添加では研削性能の向上の点から好ましくない立方結晶の析出につながり、0.05 wt% 以下では著しい効果は現われないこ

とから、0.05 wt% を超え 7 wt% に至る範囲内が適切で、特に 1~5 wt% の範囲内が最も好ましい。

なおまた、比較的少量のジルコニア量、例えは 25% タイプのアルミナージルコニア共晶体を含む研削材に対しても、上述の比較的多量のジルコニア量のアルミナージルコニア共晶体からなる研削材と同じく、正方晶ジルコニアの残存率が極めて高いことから、ジルコニアの転移点における容積変化が少なく、また残存した正方晶形ジルコニアが内部エネルギーを十分保有するに至り、良好な抗破碎性等の特性の向上が認められたものである。

次に本発明の実施例について説明する。

なお、本発明の実施例において使用する酸化イットリウム並びに酸化イットリウムを含む稀土類鉱物は第 1 表に示した分析値のものを用いた。

実施例 1.

砥粒中のジルコニアが40%となるように配合計算を行ない、バイヤー法アルミナ(99.0% Al_2O_3)50kg、ジルコニア(96% ZrO_2)32.6kgに、ジルコニアに対し重量パーセントで2.5%に相当する酸化チタン(95% TiO_2)0.8kgを混合し、さらに酸化イットリウム(99.9% Y_2O_3)を前3種の全量に対し0.05、0.1、0.5、1.2.5、5、10wt%添加して、電気炉において95V300kwで溶解し、かかる後急冷固化して各種添加量についての溶融焼成物を得た。

なお比較のために酸化イットリウムの添加量が0wt%である溶融焼成物も同条件で鋳造した。

これらの焼成物の分析値を第2表に示す。

(以下次頁)

第2表

試料番号	Y_2O_3 添加量 (wt%)	Al_2O_3	ZrO_2	TiO_2	Y_2O_3 , Fe_2O_3	SiO_2	Na_2O
1	0	56.94	41.61	1.20	—	0.05	0.12
2	0.05	57.43	41.25	1.00	0.03	0.04	0.13
3	0.1	57.91	40.75	1.05	1.06	0.05	0.14
4	0.5	57.65	40.85	1.02	0.27	0.03	0.14
5	1	57.12	40.88	1.10	0.64	0.06	0.16
6	2.5	55.92	41.30	1.03	1.52	0.05	0.14
7	5	55.16	40.45	1.05	3.09	0.04	0.18
8	10	52.47	40.12	1.11	6.05	0.05	0.17

次にこの得られた鋳造物をインペラーブレーカー及びロールクラッシャーを用いて振り返し粉碎を行ない、JIS R-6001に定められた粒度#24、#60で各々採取した。

粒度#24についてX線回折によるジルコニアの結晶形の比率を第3表に示す。

(以下次頁)

特開昭59-227726(4)

X線回折の結果明らかのように、酸化イットリウムを添加すれば、添加しない従来のアルミニウムコニアーチタニア系結晶（試料番号1）に比し、正方晶の結晶が著しく増大する傾向にあることが認められ、特に1~5wt%の添加量では100%の正方晶結晶が見出していることが認められた。また添加量が0.05wt%では一部正方晶の結晶の増大傾向はあるものの、従来のもとあまり大差なく、また10wt%を超えると立方晶の析出が認められた。

一方、この同じ粒度#24のものであって、例えば従来のもの（試料番号1）と酸化イットリウム添加量0.5wt%（試料番号3）のものとについて金属性微鏡を用いて初晶の α -Al₂O₃の析出状態を観察したところ、第1図（A）（B）及び第2図（A）（B）に示される様な結果が出た。いずれも倍率は×100で、第1図（A）（B）は試料番号1のものの拡大写真及びその模式図、第2図（A）（B）は試料番号3のものの拡大写真及びその模式図である。

1 2 3 4

試料番号	正方晶ZrO ₂ (%)	単斜晶ZrO ₂ (%)	立方晶ZrO ₂ (%)
1	30.1	69.9	0
2	32.1	67.9	0
3	70.7	29.3	0
4	87.9	12.1	0
5	100	0	0
6	100	0	0
7	100	0	0
8	85.8	0	14.2

なお両図において、1はアルミニウムコニア系結晶、2は α -Al₂O₃の初晶である。

第1図及び第2図からも明らかなるごとく、酸化イットリウムを添加したものの方は著しく α -Al₂O₃の初晶の析出が抑制されており、所定の共晶混合物が切られていることが認められた。なお他の酸化イットリウムの添加のものにあっても同様の傾向があることが確かめられているが、添加量が0.05wt%では α -Al₂O₃の析出は10%程度あり、従来のものが10~15%程度であることからすると概分その傾向が出ていているといふものの、あまり著しい差はなかった。

次に粒度#60について研削性能の試験を行なった。

すなわち研磨ベルトを作成し、研削テストを行なったものであり、その結果については第4表に示す。

なお研削テストは、使用するベルトサイズを100×2500mm/分、被研削材をSUS-304として、ベルトスピード150mm/分、圧

力5kgで、10分間研削を行なったものであり、第4表はその研削によって得られた累積研削量をもって比較したものである。

また括弧内は従来のもの（試料番号1）を100とした場合の比較値を示す。

第4表

1 2

試料番号	累積研削量 (g)
1	94.4 (Ratio 100)
2	95.0 (" 100)
3	113.0 (" 120)
4	115.7 (" 123)
5	110.2 (" 126)
6	120.6 (" 128)
7	120.4 (" 127)
8	96.0 (" 101)

また第3図における曲線（a）は、この第4表における累積研削量値をプロットしたグラフである。

る。

上記第4表あるいは第3図から明らかなように、酸化イットリウムを添加する共晶砥粒は酸化イットリウムを添加しない従来のものに比して極めて優れた研削力を發揮することが認められた。

因みにこの結果は大略第3表に示したジルコニア正方晶結晶の比率に対応しているものであって、添加量0.05wt%のものでは従来のものとあまり大差なく、1.0wt%を超えると立方晶の析出に伴い従来のものよりダウンする傾向がみられる。

しかしながら酸化イットリウムの添加は、全体としては研削力の増大傾向を若しくするものであり、しかもこのテスト結果がわずか10分間の研削時間における比較であることを考えたとき、実際の使用にあっては極めて優れた研削性能の向上に寄与し得るものである。

実施例2.

砥粒中のジルコニアが40%となるように配合計算を行ない、バイヤー法アルミナ(99.6% Al_2O_3) 50 kg、ジルコニア(96%

ZrO_2) 32.6 kgに、ジルコニアに対し重量パーセントで2.5%に相当する酸化チタン(95% TiO_2) 0.8 kgを混合し、さらに酸化イットリウムを含む粘土類結物(第1表に示す分析値のもの)を前3種の全量に対し1.

2.5、5wt%添加して、電気炉において95V、300 kwで溶融し、しかる後急冷固化して各種添加量についての溶融鉱物を得た。

これらの鉱物の分析値を第5表に示す。なお試料番号1は前記実施例1と同じく酸化イットリウム無添加の従来のものである。

(以下次頁)

第5表

試料 番号	Y_2O_3 を 合計(粘土類 結物の添加量 (wt%))	分析値						
		Al_2O_3	ZrO_2	TiO_2	＊	Fe_2O_3	SiO_2	Na_2O
1	0	56.04	41.61	1.20	—	0.05	0.12	0.08
9	1	57.36	40.97	1.04	0.42	0.05	0.13	0.03
10	2.5	56.56	41.04	1.09	1.05	0.06	0.16	0.04
11	5	56.19	40.33	1.12	2.11	0.05	0.17	0.03

＊ Y_2O_3 その他の土類

次にこの得られた鉱物をインペラーブレーカー及びロールクラッシャーを用いて繰り返し粉碎を行ない、JIS R-6001に定められた粒度#24、#60で各々採取した。

粒度#24についてX線回折によるジルコニアの結晶形の比率を第6表に示す。

(以下次頁)

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1 2 3 4

第6表

試料番号	正方晶ZrO ₂ (%)	單斜晶ZrO ₂ (%)	立方晶ZrO ₂ (%)
1	30.1	69.9	0
9	95.4	3.6	0
10	100.0	0	0
11	100.0	0	0

X線回折の結果明らかのように、酸化イットリウムを含む粘土類鉱物を添加すれば、酸化イットリウムの添加の場合と同じく、添加しないアルミニウムジルコニアチタニア系鉱粒（試料番号1）に比し、正方晶の結晶が著しく増大する傾向があることが認められ、2.5～5wt%の添加量では100%の正方晶結晶が晶出していることが認められた。

次に粒度#60について研削性能の試験を行なった。

試験条件は実施例1と同様である。その結果については第7表に示す。

第7表

1 2

試料番号	累積研削量 (g)
1	94.4 (Ratio 100)
9	118.7 (" 126)
10	120.0 (" 127)
11	119.2 (" 126)

また第3図における山線（b）はこの第7表における累積研削量値をプロットしたグラフである。

上記第7表あるいは第3図から明らかのように、酸化イットリウム添加の実施例1の場合と同様に、酸化イットリウムを含む粘土類鉱物を添加する共晶鉱粒においても優れた研削力を発揮することが認められた。

実施例3.

鉱粒中のジルコニアが40%になるように配合計算を行ない、バイヤー法アルミナ50kg、ジルコニア32.6kgにジルコニアに対して重屈パーセントで5、15wt%の酸化チタン1.7、4.9kgを混合し、酸化イットリウムを前3種の混合物に対し重屈パーセントで0.5wt%添加したものについて焼成物の分析値、粒度#24についてのX線回折によるジルコニア結晶形の比率及び粒度#60についての累積研削量を測定した。

その結果をそれぞれ第8表、第9表及び第10表に示す。

なお比較のため、酸化チタン2.5wt%の添加

量のもの、及びそれぞれのチタニア添加量のものについての酸化イットリウム無添加の場合の値も併記した。

また試験方法はいずれも実施例1及び実施例2と同様である。

（以下次頁）

特圖號59-227726(7)

第 8 章

試験 番号	Ti O ₃ 量/重量 (%)	Y ₂ O ₃ 量/重量 (%)	Al ₂ O ₃	Zr O ₃	Ti O ₃	Y ₂ O ₃	Fe ₂ O ₃	Si O ₂	Na ₂ O
1	2.5	0	56.94	41.61	1.20	—	0.05	0.12	0.00
4	2.5	0.5	57.05	40.85	1.02	0.27	0.03	0.14	0.04
12	5	0	57.06	40.63	2.06	—	0.03	0.16	0.04
13	5	0.5	56.78	40.71	2.04	0.25	0.04	0.15	0.03
14	15	0	54.16	39.72	5.91	—	0.03	0.14	0.04
15	15	0.5	53.41	40.24	5.83	0.28	0.04	0.15	0.04

第9表

試料番号	正方晶 ZrO ₂		單斜晶 ZrO ₂	
	(%)		(%)	
1	30.1		69.9	
4	87.9		12.1	
12	33.0		67.0	
13	90.2		9.8	
14	34.2		65.8	
15	93.6		6.4	

三 10 製

試料番号	吸粘研削量(μ)
1	94.4 (Ratio 100)
4	115.7 (" 123)
12	95.0 (" 100)
13	112.5 (" 119)
14	92.0 (" 97)
15	117.3 (" 124)

上記表からも明らかのように、酸化チタンの添加量の増加に従い正方晶 ZrO_2 の残存率は増大傾向を示しているが、それにも増して酸化イットリウムの添加による著しい増大傾向が認められた。またこれに対応して研削力の増大傾向が累積研削品の酸化結果から認められる。

实施例4.

砥粒中のジルコニアが25%並びに32%になるように配合計算を行ない、バイヤー法アルミニウム(99.6%Al₂O₃)150kg並びに24.5kg、ジルコニア(96%ZrO₂)16.6kg並びに11.5kgに、ジルコニアに対して、重量パーセントで0.2.5.5.10.15.20.30.40%の酸化チタン(95%TiO₂)を各々添加したものと、砥粒中のジルコニアが25%になるように配合計算を行ない、バイヤー法アルミニウム(99.6%Al₂O₃)150kg、ジルコニア(96%ZrO₂)16.6kgに、ジルコニアに対して重量パーセントで0.5.10.15.20.

30、40%の酸化チタン(9.5% TiO₂)を
添加し、さらに酸化イットリウムを前3種の物質
全量に対して0.5wt%添加したものをそれぞれ、
電気炉を用いてアーク熱で溶融・急冷固化し、こ
れを一般的な砥粒の生産方式に従って粒粒し、
JIS #12の砥粒とした。

これらのもの、すなわち酸化イットリウム無添加のジルコニア 25% タイプ及び 32% タイプのものと、酸化イットリウム添加のジルコニア 25% タイプのものについて抗破壊性測定試験を行なった。抗破壊性測定には単粒圧壊強度を用いた。この方法は、試料を 1680~2000 ミクロンに粒度して、粒分法により小試料とし、その中からランダムに 100 個採取して、これを 2 トニアムスラー圧縮器で 1 回ずつ耐圧強度を測定して、その平均値を単粒圧壊強度とした。

これらの砥粒の単粒圧壊強度を第11表に、単粒圧壊強度と TiO_2 / ZrO_2 との関係を第4図に示す。

第 11 表

試験番号	タイプ	TiO ₂ / ZrO ₂ (%)							
		0	2.5	5	10	15	20	30	40
16	Y ₂ O ₃ 無添加 ZrO ₂ 25% タイプ	46.0	48.8	51.9	61.0	60.0	58.9	52.2	46.7
17	Y ₂ O ₃ 無添加 ZrO ₂ 32% タイプ	46.3	47.5	53.8	83.0	63.3	62.0	49.3	46.0
18	Y ₂ O ₃ 無添加 ZrO ₂ 25% タイプ	48.1	—	55.8	64.7	64.2	63.3	54.1	48.0

第4図より明らかなる様に、いずれのタイプにおいても TiO₂ / ZrO₂ が重量パーセントで 10 ~ 20% の範囲内で、max 値を示し、40%になると低下するが、特に酸化イットリウムを添加したものについては、ZrO₂ 25% タイプにあっては勿論、32% タイプと比較しても更にすぐれた抗破碎性を發揮することが認められた。

以上のとくこの発明は、アルミナにジルコニア及びチタニアを添加溶融し、急冷してなるアルミナジルコニアチタニア系研削材において、さらに他の溶融添加物として酸化イットリウムまたは酸化イットリウムを含む粘土類鉱物を含有させることにより、研粒中にジルコニア正方晶結晶を最大 100% 存在させたものであり、また比較的ジルコニア量の多いアルミナジルコニア共晶体からなる研削材にあって初品の α -Al₂O₃ の析出を 5% 以下に抑えたもので、研削性能を著しく向上させた研削材を提供し得たものである。

従って粗研削の中でも特にその粗研削に対し、またさらにチタン合金に対して格別に良好に適応

して使用できるものである。

また比較的ジルコニア量の少ないアルミナジルコニア共晶体を含む研削材にあっても従来に比較すればその抗破碎性等の特性において一段と向上し得たものである。

4. 図面の簡単な説明

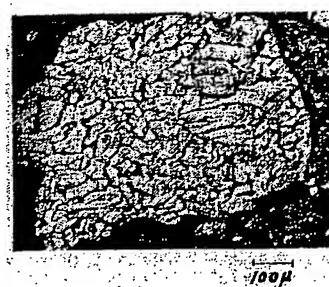
第1図 (A) (B) は従来の酸化イットリウム無添加のアルミナジルコニア共晶混合物 (試料番号1) の拡大写真及びその模式図。

第2図 (A) (B) はこの発明の一実施例である酸化イットリウム添加のアルミナジルコニア共晶混合物 (試料番号3) の拡大写真及びその模式図。

第3図は四次低例及び他次低例である酸化イットリウム添加の研削材及び酸化イットリウムを含む粘土類鉱物添加の研削材における酸化イットリウム等の添加量と研削剤量の関係図。

第4図はジルコニア量が比較的少ない研削材における酸化チタンの添加量と単粒圧壊強度との関係図である。

第1図 (A)

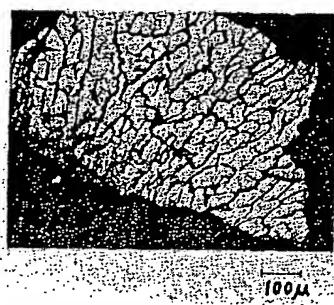


(B)

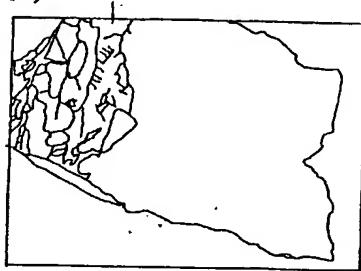


第2図

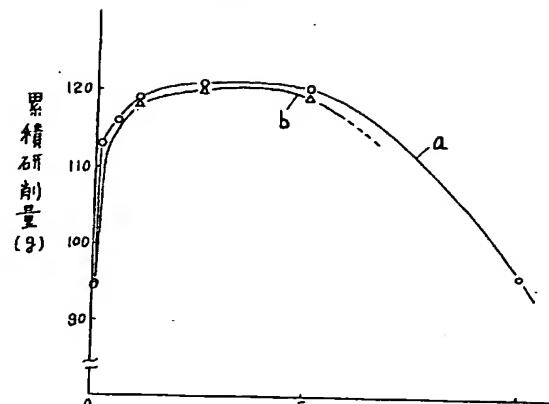
(A)



(B)



第3図

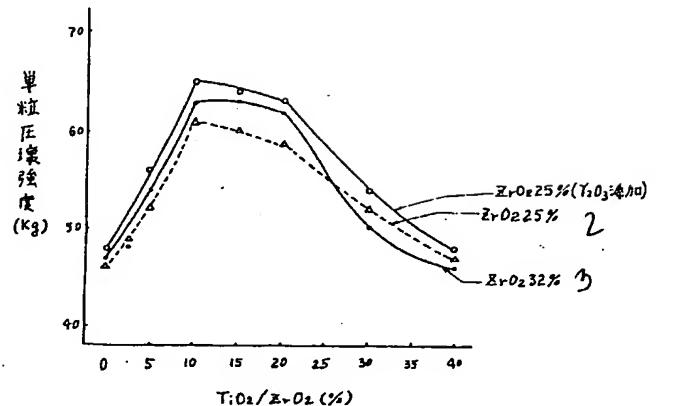


Y₂O₃若しくはY₂O₃を含む稀土類鉱物の添加量(wt%)

(a) …… Y₂O₃の添加

(b) …… Y₂O₃を含む稀土類鉱物の添加

第4図



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